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# Hydrogen storage properties of Zr-based multicomponent alloys with C14-Laves phase structure derived from the Zr–Cr–Mn–Fe–Ni system

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#### ABSTRACT

This study focused on assessing the crystal structure and hydrogen storage properties of two multicomponent alloys having the  $Zr_{33}$ (CrMnFeNi)<sub>67</sub> and  $Zr_{33}$ Cr<sub>22</sub>Mn<sub>15</sub>Fe<sub>25</sub>Ni<sub>5</sub> compositions. Both alloys were designed by thermodynamic calculations derived from the TiZrCrMnFeNi system after removing the titanium element from the original composition and keeping the high fraction of zirconium to explore new Zr-based compositions with a strong tendency to crystallize as a C14 Laves phase. The arc-melted Zr-based alloys exhibited a significant presence of C14 Laves phases and small amounts of NiZr intermetallic phase. Hydrogen storage properties investigated through pressure-composition-temperature (PCT) absorption and desorption isotherms revealed that the  $Zr_{33}Cr_{22}Mn_{15}Fe_{25}Ni_5$  alloy could absorb 1.8% (H/M = 1.2) of hydrogen with fast kinetics at room temperature after a simple heat activation, while the  $Zr_{33}(CrMnFeNi)_{67}$  alloy could reversibly absorb 1.6% (H/M = 1) with equally fast kinetics. Zr-rich alloys exhibited a low hydrogen equilibrium pressure in the PCT isotherms. After full hydrogenation at room temperature, the initial metallic C14 Laves phases were converted to the respective Laves phase hydrides in both cases. Under cycling, the fractions of the secondary NiZr and the C14 phase change as the samples become more activated. The microstructural analysis, before and after the cycling, showed a very homogeneous microstructure and good distribution of the elements in both alloys.

## 1. Introduction

In the last few decades, high-entropy alloys (HEAs) have attracted much attention in the materials science field due to their remarkable structural and functional properties, including hydrogen storage [1–6]. As a brief definition, HEAs are defined as multi-principal element alloys composed of five or more principal elements with a ratio between 5 and 35 at% [7–18]. In the field of hydrogen storage, HEAs are also called high-entropy hydrides (HEHs) and are considered a new class of potential hydrogen storage materials for solid-state storage applications [19–34]. After the first publication in 2010 [19] showing very interesting hydrogen storage properties from several HEHs derived from the CoFeMnTi<sub>x</sub>V<sub>y</sub>Zr<sub>z</sub> ( $0.5 \le x \le 2.5, 0.4 \le y \le 3.0$  and  $0.4 \le z \le 3.0$ ) system, for the CoFeMnTiVZr<sub>2.3</sub> alloy, the number of studies on this issue has dramatically increased over the last years [3].

One of the main challenges in the hydrogen storage field is to find a suitable material or a hydride that can be able to simultaneously satisfy a

several list of criteria such as (most relevant): the capability for reversible absorption and desorption of hydrogen at room temperature, fast kinetics, easy-activation, high cycling stability, appropriate storage pressure near atmospheric pressure and high gravimetric capacity [2,3]. As those hydrogen storage properties are very sensitive to the alloy composition, the HEHs possess a huge composition field to be explored offering endless possibilities for tuning the hydrogen storage properties [4,14]. The vast compositional space of HEAs has been explored by using thermodynamic-based design methods such as semi-empirical rules, *ab-initio* calculations, and CALPHAD (Calculation of Phase Diagrams) [17,18]. Those methods are being used to provide a more fundamental understanding of the phases and their stability that could be present in HEAs which allow us to associate with a certain desired feature for hydrogen storage properties.

Recently, multicomponent alloys with C14 Laves phase structure have attracted much attention as a potential hydride for solid-state storage due to its good hydrogen storage capacity at room

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temperature, fast kinetics, and excellent reversibility without applying a complex activation procedure [7-14]. To select new multicomponent alloys with C14 Laves phase structure, a set of criteria has been proposed [5]. More specifically, three criteria were proposed to design high-entropy alloys for room temperature hydrogen storage: total valence electron concentration (VEC) of 6.4, single-phase thermodynamic stability (examined by CALPHAD calculations) and the choice for an alloy with an AB<sub>2</sub>H<sub>3</sub> hydride formation stoichiometry [10]. In this context, the selected TiZrCrMnFeNi alloy reported in our previous study [10] showed excellent reversibility and high hydrogen sorption capacity (over 1.6 wt%) at room temperature without any previous activation. Considering the successful results of applying this set of criteria, for TiZrCrMnFeNi alloy, it is clear the necessity to go deeper on this issue, allowing to find new promising compositions with C14 Laves phases structure in the vast multi-elemental composition field by combining with computational semi-empirical methods thermodynamic calculations.

Mostly the C14-based alloys reported so far with a focus on hydrogen storage applications not only showed very good hydrogen storage properties at room temperature [7,11-13], but also their behavior at moderate temperatures has been investigated [10–13]. In our previous publications [12,13], the hydrogen storage properties of the current TiZrNbCrFe and TiZrNbCrFeNi alloys were studied at moderate temperatures. For TiZrNbCrFeNi alloy, the PCT absorption and desorption isotherms for two cycles were conducted at different temperatures of 303 K, 353 K, 373 K, and 473 K, subsequently. The microstructural characterization showed the presence of two C14 phases differentiable only by the lattice parameters (C14#1 and C14#2). Although there was not any improvement in the hydrogen absorption at intermediate temperatures (353 K and 373 K) in comparison with room temperature (303 K), at 473 K the initial metallic C14#1 and C14#2 phases presented in the as-cast alloy were entirely converted into their respective hydrides, so both C14 phases became indistinguishable. Furthermore, the observed decrease of the hydrogen capacity at 303 K between the first and the second cycle did not occur at 473 K. The two complete cycles at 473 K absorbed and desorbed the same amount of hydrogen.

Regarding the multicomponent nature of the referred alloys TiZrCrMnFeNi, TiZrNbFeNi, TiZrNbCrFe, and TiZrNbCrFeNi reported in our previous studies [10–13], the role of each element concerning their chemical affinity with hydrogen must also be investigated, which could be useful to restrict the compositional field and, finally, select more promising alloys for solid-state hydrogen storage. In this sense, the effect of different atomic percentages of titanium and zirconium has been recently studied in the  $Ti_xZr_{1-x}CrMnFeNi$  system [14]. On the



fundamental aspect of the crystalline structures, the authors claimed that the change in the percentages of hydride formation elements – such as titanium and zirconium – affected the hydrogen binding energy, which is the most important parameter that needs to be adjusted for reversible hydrogen storage at room temperature and under atmospheric pressures. The designed alloys –  $Ti_xZr_{1-x}CrMnFeNi$  – reversibly absorb and desorb at room temperature while the equilibrium pressure can be adjusted by controlling the hydrogen binding energy. The equilibrium pressure can be reduced to low values by reducing the hydrogen binding energy to more negative values increasing the zirconium atomic fraction. Additionally, variating the atomic percentage of zirconium and titanium keeps the VEC close to 6.4, which is favorable for low-temperature hydrogen storage [10–12].

Inspired by the remarkable hydrogen storage results of TiZrCrMn-FeNi alloy at room temperature, in this study, the crystal structure and the hydrogen storage properties of Zr<sub>33</sub>(CrMnFeNi)<sub>67</sub> and Zr<sub>33</sub>Cr<sub>22</sub>Mn<sub>15</sub>Fe<sub>25</sub>Ni<sub>5</sub> high entropy alloys were investigated. These two Zr-based alloys were designed by thermodynamics calculations using the CALPHAD method following three main criteria: i) to explore the compositional field of Zr-Cr-Mn-Fe-Ni system without the presence of titanium, mainly due to its high stability with hydrogen and high trend to increase the hydrogen plateau pressure [14]; ii) looking for Zr-based alloys with single phase or high tendency to form the intermetallic C14 Laves phases [9]; iii) keeping the VEC parameter close to 6.4 [10–12]. The alloys were produced by arc melting under an argon atmosphere and studied by detailed structural and microstructural characterizations. Hydrogen storage properties at room temperature have been also systematically investigated, as well as the effect of the high concentration of zirconium concerning the behavior of the isotherm PCT curves, especially in the plateau equilibrium pressure.

#### 2. Experimental

The Zr-based high entropy alloys, namely  $Zr_{33}(CrMnFeNi)_{67}$  and  $Zr_{33}Cr_{22}Mn_{15}Fe_{25}Ni_5$ , were synthesized through arc melting of highpurity elemental chips and pieces of Zr (99.5%), Cr (99.99%), Mn (99.99%), Fe (99.97%), and Ni (99.99%). The arc melting process was carried out using a non-consumable tungsten electrode and a watercooled copper crucible within a high-purity argon atmosphere. To improve chemical homogeneity, the ingots were rotated and remelted six times. The mass loss resulting from the arc melting process was found to be less than 1%. Subsequently, the arc-melted ingots were sectioned into small pieces for further characterization.

For crystal structure analysis, the alloy samples were crushed into micro-sized powders and subjected to X-ray diffraction (XRD) measurements. XRD analysis was performed using a Cu-Ka radiation source  $(\lambda = 0.15406 \text{ nm})$  with an X'Pert Panalytical diffractometer equipped with a graphite monochromator and operating at 45 kV and 40 mA. Rietveld refinement method in conjunction with GSAS-II software was employed to determine lattice parameters, phase fractions (wt.%), crystallite size, and isotropic microstrain. The refinement process involved the adjusting of the following parameters: 1) background estimation using a Chebyshev background function with 5 coefficients, 2) determination of phase fractions, 3) refinement of lattice parameters, 4) estimation of crystallite size, and 5) determination of isotropic microstrain. No instrumental parameters were refined during these analyses. The obtained refinements exhibited residual values (Rwp) and goodness-of-fit (GOF) below 5%, indicating the high quality and reliability of the results [33].

Microstructural studies were conducted by using scanning electron microscopy (SEM). The samples were mechanically polished using colloidal silica with a particle size of 60 nm. The polished samples were examined using a scanning electron Philips XL-30 FEG microscope equipped with energy-dispersive X-ray spectroscopy (EDS). Backscattered electron and secondary electron (BSE and SE) images together with elemental mapping at different magnifications in selected



Fig. 2. Fraction of equilibrium phases as a function of temperature calculated for the  $Zr_{33}Cr_{22}Mn_{15}Fe_{25}Ni_5$  alloy using CALPHAD and TCHEA3 database.

#### Table 1

Calculated composition and constitution of the equilibrium phases of the equiatomic Zr33(CrMnFeNi)67 alloy at 1000  $^\circ\text{C},$  using Thermo-Calc with TCHEA3 database.

Phase	Element at%		Constitution A Site Fraction		Constitution B Site Fraction	
C14	Zr	32.1	Zr	1	Zr	-
$AB_2$	Mn	17.3	Mn	-	Mn	0.41
	Fe	17.6	Fe	-	Fe	0.33
	Cr	18.0	Cr	-	Cr	0.16
	Ni	15.0	Ni	-	Ni	0.1
NiZr	Zr	0.5	Zr	1	Zr	-
AB	Ni	0.5	Ni	-	Ni	1

regions were taken in all samples.

To evaluate the hydrogen storage performance, PCT (pressurecomposition-temperature) absorption and desorption isotherms, as well as kinetic measurements, were conducted at room temperature. Samples with around ~250 mg weight were crushed in an argon-filled glove box to reduce the particle size below 100  $\mu$ m. The measurements were carried out by using a Sievert-type apparatus SETARAM® PCT-Pro model. Before starting the measurements at room temperature, an activation process was performed. The activation procedure consisted of keeping the sample under a dynamic vacuum at 450 °C for 3 h and immediately cooling it down to room temperature.

#### 3. RESULTS and DISCUSSION

#### 3.1. - Thermodynamic calculation and structural characterization

Fig. 1 shows the fraction of equilibrium phases as a function of temperature for the equiatomic  $Zr_{33}$ (CrMnFeNi)<sub>67</sub> alloy, calculated by the CALPHAD method using the TCHEA3 database and the Thermo-Calc software. As observed in Fig. 1, it is quite clear that under the equilibrium thermodynamic conditions, the alloy begins to crystallize the primary C14#1 Laves phase followed by a secondary C14#2 and NiZr intermetallic phases after a complete solidification at approximately 1000 °C. By considering that all solidification of alloy should finish at 1000 °C and keep unaltered till room temperature, the alloy is expected to possess 92% of the C14 Laves phase and 8% of the NiZr phase. Fig. 2 shows the thermodynamic calculations performed by the same method described before for the  $Zr_{33}Cr_{22}Mn_{15}Fe_{25}Ni_5$  alloy. In contrast to the first alloy, it is expected an almost full crystallization of the C14 Laves phase at a relatively high temperature, which amount decreases with the



Fig. 3. XRD profile and Rietveld refinement of  $Zr_{33}$ (CrMnFeNi)<sub>67</sub> alloy in the as-cast state.

#### Table 2

Crystal structure of the phases used for Rietveld refinement of the Zr33 (CrMnFeNi)67 and Zr33Cr22Mn15Fe25Ni5 alloys.

Phase	Sublattice	Wyckoff position	Atom	Occupation factor
C14 Space Group:	Α	4f (1/3, 2/3, 0.06030)	Zr	1
P63/mmc (194)	В	2a (0, 0, 0)	Mn Fe Cr Ni	0.41 0.33 0.16 0.1
	В	6h (0.83170, 0.66340, 1/4)	Mn Fe	0.41
			Ni	0.10
NiZr Space Group:	A	4c (0, 0.08170, 0.25)	Zr	1
Cmcm (63)	В	4c (0, 0.36090, 0.25)	Ni	1

temperature reduction. Despite the high tendency of formation of the C15 Laves phase at low temperatures, the formation of a major quantity of the C14 Laves phase seems plausible.

Table 1 shows the calculated chemical composition of the equilibrium phases at 1000  $^{\circ}$ C as well as their sublattice constitution for the Zr<sub>33</sub>(CrMnFeNi)<sub>67</sub> alloy. The composition and structure of C14 and cubic

#### Table 3

Lattice parameters, phase fractions, crystallite size, and isotropic microstrain of the phases obtained by Rietveld refinement for Zr33 (CrMnFeNi)67 alloy in the as-cast state.

Phases	Lattice Parameters (Á)	Phase Fraction (wt. %)	Crystallite Size (µm)	Microstrain ( $\Delta d$ / d) $\times 10^6$
C14	a = 5.01138 c = 8.20292 Vol = 178.408 Å <sup>3</sup>	91.2	10	5421.7
NiZr	a = 3.27408 b = 9.95311 c = 4.08681 Vol = 133.178 Å <sup>3</sup>	8.8	0.3865	15408.1



Fig. 4. XRD profile and Rietveld refinement of  $\rm Zr_{33}Cr_{22}Mn_{15}Fe_{25}Ni_5$  alloy in the as-cast state.

#### Table 4

Lattice parameters, phase fractions, crystallite size, and isotropic microstrain of the phases obtained by Rietveld refinement for Zr33Cr22Mn15Fe25Ni5 alloy in the as-cast state.

Phases	Lattice Parameters (Á)	Phase Fraction (wt. %)	Crystallite Size (µm)	Microstrain ( $\Delta d$ / d) $\times$ 10 <sup>6</sup>
C14	a = 5.02155 c = 8.23092 Vol = 179.744 Å <sup>3</sup>	98.4	0.4477	3326.8
NiZr	a = 3.268 b = 9.937 c = 4.101 Vol = 133.176 Å <sup>3</sup>	1.6	2.4034	9574.5

phases are described in Table 1, where the constitution of the first C14type Laves phase is  $(Zr)(Cr_{0.16}Mn_{0.41}Fe_{0.33}Ni_{0.1})$  and the intermetallic phase is an orthorhombic ordered structure with the constitution of (Ni) (Zr).

Fig. 3 shows the experimental XRD pattern and the Rietveld refinement of the  $Zr_{33}$ (CrMnFeNi)<sub>67</sub> alloy in the as-cast state (Rwp = 3.56). The compositions and constitutions presented in Table 1 were used as a basis for building the crystal structure of the C14 Laves phases to be used in the Rietveld refinements in both alloys, as shown in Table 2. As seen in Fig. 3, the as-cast structure of  $Zr_{33}$ (CrMnFeNi)<sub>67</sub> alloy could be well fitted by using one crystal structure of hexagonal C14-type Laves phase. It can also be noted the presence of reflections related to the intermetallic NiZr, which is in accordance with the prediction in the thermodynamic calculation under the equilibrium conditions as discussed before. Table 3 gives the lattice parameters, phase fractions, crystallite size, and isotropic microstrain of the C14-type Laves and the intermetallic phases resulting from the Rietveld refinement carried out in the  $Zr_{33}$ (CrMnFeNi)<sub>67</sub> alloy.

In concern to the possible presence of a second C14-type Laves phase, as suggested by the thermodynamic calculations, it was not possible to differentiate these two phase types from the diffraction pattern, so it was the reason why the Rietveld refinement was held only with one of crystal structure.

Fig. 4 shows the experimental XRD pattern and the Rietveld refinement for the second Zr-rich alloy with the  $Zr_{33}Cr_{22}Mn_{15}Fe_{25}Ni_5$  composition (Rwp = 3.35). Similarly, to the first Zr-rich alloy, the experimental XRD can be well fitted by using one crystal structure of C14 type Laves phase. Furthermore, it can be noted the presence of reflections of the intermetallic NiZr phase, which is possibly present in this alloy. Table 4 summarizes the lattice parameters, phase fractions, crystallite size, and isotropic microstrain of the obtained Rietveld refinement of the Zr<sub>33</sub>Cr<sub>22</sub>Mn<sub>15</sub>Fe<sub>25</sub>Ni<sub>5</sub> alloy. The evaluation of the values of lattice parameters indicated in Tables 3 and 4, respectively for the Zr<sub>33</sub>(CrMnFeNi)<sub>67</sub> and Zr<sub>33</sub>Cr<sub>22</sub>Mn<sub>15</sub>Fe<sub>25</sub>Ni<sub>5</sub> alloys showed a very similar C14 unit cell, which can be explained by the approximate composition and site occupancy of each element, beyond that both alloys are made of the same elements. Minimal differences in the crystallite size and microstrain can be attributed to the chemical gradient as a result of the casting process. It should be mentioned that the same explanation can be extended to the minor intermetallic NiZr phase, in terms of structural parameters. In controversy, the absolute phase fraction of NiZr is significantly lower in the Zr<sub>33</sub>Cr<sub>22</sub>Mn<sub>15</sub>Fe<sub>25</sub>Ni<sub>5</sub>, which is consistent with the lesser amount of Ni (5% atomic) in the alloy. Nevertheless, the C14 is the main phase for both alloys, corresponding to over 90% in mass, as suggested by Thermo-Calc predictions. Not less important, the VEC of the alloys, 6.5 and 6.2, respectively, for the Zr<sub>33</sub>(CrMnFeNi)<sub>67</sub> and Zr<sub>33</sub>Cr<sub>22</sub>Mn<sub>15</sub>Fe<sub>25</sub>Ni<sub>5</sub> are close to the 6.4 appointed as a favorable condition for C14 crystallization [10–12].

#### 3.2. - Microstructural characterization

Fig. 5a-c shows SEM images including the EDS elemental mappings of the selected elements for the alloy Zr<sub>33</sub>(CrMnFeNi)<sub>67</sub> in the as-cast state. It is possible to observe from the SEM images (Fig. 5a in BSE mode and Fig. 5b in SE mode) two distinct regions, a bright region, homogeneously distributed in the shape of filaments through a second darker region, much more abundant, characterized as the matrix of the microstructure. From the EDS elementary mapping, as shown in Fig. 5c, the brighter areas are composed of Zr and Ni, which is consistent with the higher atomic mass of Zr, indicating the presence of the intermetallic NiZr phase in the interdendritic region. This observation is in full agreement with the phases found in the XRD analysis presented in Fig. 3. Zr is also nearly homogeneously distributed over the microstructure, except in the presence of some regions with a brighter red, where Zr is in higher concentration. The other elements, i.e., Fe, Mn, and Cr are present only in the matrix, meanwhile, Ni is present in both phases. With attentive analysis of Fig. 5a-c and the phase diagram of the alloy, in Fig. 1, one can infer that the intermetallic NiZr is the last phase to nucleate, due to the partial segregation of Zr to the interdendritic space, combining with Ni to form NiZr. That said, the dendritic areas that correspond to the matrix are the C14 Laves phase, the first one to nucleate from the liquid state in solidification. Ultimately, the EDS spectrum shown in Fig. 5d, reveals that the atomic fraction of elements is very close to the nominal fraction of alloy, and, to the C14 phase composition predicted in Table 1, revealing negligible misbalance or loss during the arc melting process.

In Fig. 6a–c is observed the SEM images as well EDS elemental mappings of the second alloy,  $Zr_{33}Cr_{22}Mn_{15}Fe_{25}Ni_5$ . The general aspect of the microstructure is quite similar to the first alloy since both alloys contain the same elements in different atomic proportions. From Fig. 6a–b it is evident the existence of bright areas over a dark background, which indicates a heavier element-rich phase. The nature of this phase is elucidated by the EDS images in Fig. 6c, unquestionably composed of Zr and Ni, compatible with the intermetallic NiZr phase also identified in the XRD analysis (Fig. 4). However, considering the same magnification of the BSE images from the two alloys, visually the  $Zr_{33}Cr_{22}Mn_{15}Fe_{25}Ni_5$  alloy has a lesser amount of intermetallic phase, which agrees with the phase fraction in mass obtained by the Rietveld refinement, as seen in Tables 3 and 4. Despite this clear result, it should be taken into account that the phase fraction of NiZr and C14 obtained could not be accurate, since the existence of heterogeneities on the





**Fig. 5.** SEM images and corresponding EDS elemental mappings of  $Zr_{33}$ (CrMnFeNi)<sub>67</sub> alloy in the as-cast state. **a**) SEM images using the back-scattered electrons. **b**) SE image. **c**) EDS elemental mappings with selected elements Zr, Mn, Fe, Cr, and Ni **d**) EDS spectrum (intensity versus energy) obtained from image (c) showing the atomic fraction (at%) of elements.

microstructure in the as-cast state as a result of the arc melting process.

Not less important, in both sets of BSE images of the two alloys, it is also evident the presence of porosities and microcracks which are certainly associated with the fragile nature of the intermetallic C14 Laves phase present in high proportions.

# 3.3. - Hydrogen storage examination by PCT, structural and microstructural analysis

The alloys,  $Zr_{33}$ (CrMnFeNi)<sub>67</sub> and  $Zr_{33}Cr_{22}Mn_{15}Fe_{25}Ni_5$ , were evaluated for the hydrogen storage performance by PCT absorption/ desorption isotherms and kinetics carried out at room temperature. These two alloys are derivates from the equiatomic TiZrCrMnFeNi reported in our previous paper [10], which displayed a hydrogen capacity of 1.7 wt% reversibly at room temperature and fast kinetics without any activation process. For both alloys of this study, it was necessary a previous single activation process to start absorbing hydrogen, which consisted of heating the samples at 450  $^\circ \rm C$  for 3 h in a dynamic vacuum followed by cooling down to room temperature to initiate the measurements.

Fig. 7 shows the first kinetic absorption curves measured under 25 bar of H<sub>2</sub> at room temperature (298 K). It can be seen very similar behavior on the kinetic curves of the two Zr-rich alloys, considering the amount of hydrogen absorbed over time (maximum amount absorbed: H/M = 1.09 and H/M = 1.04). The hydrogen absorption time to 90% of total mass, t<sub>0.9</sub>, is slightly lower for Zr<sub>33</sub>Cr<sub>22</sub>Mn<sub>15</sub>Fe<sub>25</sub>Ni<sub>5</sub> compared to Zr<sub>33</sub>(CrMnFeNi)<sub>67</sub>. More specifically, these values are, respectively, 54 s and 165 s. By far, both alloys presented faster kinetics compared to the equiatomic TiZrCrMnFeNi alloy, with t<sub>0.9</sub> = 1800 s. This result can be attributed to the higher concentration of Zr and the absence of Ti since Zr has higher absolute hydrogen enthalpy of formation than Ti (ZrH<sub>2</sub> = -162.8 kJ/mol.H<sub>2</sub>; TiH<sub>2</sub> = -123.8 kJ/mol.H<sub>2</sub>) [35]. However, it is possible the TiZrCrMnFeNi alloy could have shown similar results if applicated the same activation temperature of 450 °C for 3 h under



**Fig. 6.** SEM images and corresponding EDS elemental mappings of Zr<sub>33</sub>Cr<sub>22</sub>Mn<sub>15</sub>Fe<sub>25</sub>Ni<sub>5</sub> alloy in the as-cast state. **a)** SEM images using the back-scattered electrons. **b)** SE image. **c)** EDS elemental mappings with selected elements Zr, Mn, Fe, Cr, and Ni.



Fig. 7. Kinetics curves of the two Zr-rich alloys and the correspondent equiatomic TiZrCrMnFeNi alloy at 25 bar and room temperature.

vacuum.

After the kinetics measurements, the alloys were heated again to 450 °C for 3 h in a dynamic vacuum, to desorb any residual hydrogen. Figs. 8 and 9 show, respectively, the PCT cycles of absorption and desorption of  $Zr_{33}(CrMnFeNi)_{67}$  and  $Zr_{33}Cr_{22}Mn_{15}Fe_{25}Ni_5$  alloys at room temperature. Firstly, by looking at both PCT absorption and desorption isotherms is evident the presence of a well-defined equilibrium plateau pressure. This feature is an indication that the hydrogen absorption mechanism probably occurred by interstitial solid solution ( $\alpha$ -phase) and hydride nucleation ( $\beta$ -phase). Secondly, both alloys start to absorb hydrogen at very low pressure, of the order of kilopascal. We were unable to fully assess the kinetic behavior (desorption kinetic) of the Zr-alloys under study. As depicted in Figs. 8 and 9, the equilibrium plateau pressure of these alloys is lower than  $10^{-1}$  MPa and is close to  $10^{-2}$  MPa. This implies that desorption occurs at low pressures, which is out of the detection limit of the apparatus.

The  $Zr_{33}$ (CrMnFeNi)<sub>67</sub> alloy absorbs 1.6 wt% of hydrogen (H/M = 1.08) and desorbs 1.43 wt% of hydrogen (H/M = 0.96) in the first cycle.



Fig. 8. PCT curves of hydrogen absorption/desorption for the AB2-type  $Zr_{33}$ (CrMnFeNi)<sub>67</sub> at room temperature.

In desorption, when the pressure reaches  $10^{-2}$  MPa to  $10^{-4}$  MPa, an asymptotic behavior of the isotherm curve can be observed, indicating the presence of retained hydrogen in the C14 phase. However, this amount corresponds only to 10% of the total absorbed, which is expected for AB<sub>2</sub> high entropy alloys [10–14].

The Zr<sub>33</sub>Cr<sub>22</sub>Mn<sub>15</sub>Fe<sub>25</sub>Ni<sub>5</sub> alloy showed an even better performance in terms of hydrogen capacity at the maximum hydrogen pressure (5 MPa for both alloys). The alloy was able to reversibly absorb 1.8 wt% of hydrogen with a maximum of 1.22 *H/M* ratio and desorb 1.6 wt% corresponding to a 1.08 *H/M* ratio. There were no differences in terms of reversibility when compared to the first alloy. The equilibrium plateau pressure was half of the first one and can be explained by the differences in the concentration of B elements, once the alloys have the same amount of Zr. Regardless of any differences in the plateau pressure, the ability of Zr to reduce the equilibrium plateau is evident and aligned with the results described in other alloys with high concentrations of Zr



Fig. 9. PCT curves of hydrogen absorption/desorption for the  $AB_2\mbox{-type}\ Zr_{33}Cr_{22}Mn_{15}Fe_{25}Ni_5$  at room temperature.



Fig. 10. XRD profile and Rietveld refinement of  $Zr_{33}(CrMnFeNi)_{67}$  alloy after hydrogenation at room temperature.

### [9,14].

The crystal structure of the hydrogenated state of the alloys has also been investigated by XRD followed by Rietveld refinement. As shown in Fig. 10 (Rwp = 1.31), the C14 Laves phase of the  $Zr_{33}$ (CrMnFeNi)<sub>67</sub> alloy has been fully converted to a hydride C14, which is proven by the shift of the peaks to lower angular positions compared to Fig. 3. This also

indicates the stability of the hydride phase at atmospheric pressure, once the sample was opened to the atmosphere to perform the XRD experiment. Table 5 summarizes the lattice parameters, phase fraction, crystallite size, and isotropic microstrain of the phases determined by Rietveld refinements after hydrogenation. Firstly, it can be confirmed the formation of the C14 hydride phase by the significant increase of the lattice parameters and the unit cell volume (up to 18% compared to the as-cast state). On the other hand, the phase fraction has not significantly changed compared to the as-cast state. The NiZr intermetallic phase has not changed in terms of lattice parameters and phase fraction after hydrogenation, attesting that the second phase has no role in the hydrogenation process.

Fig. 11 shows the XRD pattern of the hydrogenated state of the  $Zr_{33}Cr_{22}Mn_{15}Fe_{25}Ni_5$  alloy (Rwp = 1.32). The hydride C14 phase is largely present after hydrogenation as well. For this sample, the refinement was done without including the intermetallic NiZr phase identified in the XRD pattern (Fig. 4), as its presence is lower than 2% in the as-cast state. A direct comparison between Tables 5 and 6 reveals that the lattice parameters of the majority C14 Laves phase and consequently the volume per unit cell of both alloys increased after hydrogenation. They have approximately the same values after the respective hydrogenation, except for a slightly higher unit cell volume for the Zr<sub>33</sub>Cr<sub>22</sub>Mn<sub>15</sub>Fe<sub>25</sub>Ni<sub>5</sub> in comparison to Zr<sub>33</sub>(CrMnFeNi)<sub>67</sub> alloy. However, under cycling, the phase fraction of the C14 hydride phase in the Zr<sub>33</sub>Cr<sub>22</sub>Mn<sub>15</sub>Fe<sub>25</sub>Ni<sub>5</sub> alloy reaches 100%, which explains its superior hydrogen storage capacity. This can be attested by the decrease in the amount of the intermetallic NiZr after hydrogenation (negligible quantities) compared to the as-cast (1.6%) as seen, respectively, in Tables 6 and 4. The change in the amount of NiZr can be explained by the lattice distortion after hydrogenation, the amount of NiZr in the hydrogenated



Fig. 11. XRD profile and Rietveld refinement of  $Zr_{33}Cr_{22}Mn_{15}Fe_{25}Ni_5$  alloy after hydrogenation at room temperature.

#### Table 5

Lattice parameters, phase fraction, crystallite size, and isotropic microstrain of the phases obtained by Rietveld refinement for Zr33(CrMnFeNi)67 alloy after hydrogenation at 296 K.

Phases	Lattice Parameters (Á)	Phase Fraction (wt.%)	Crystallite Size (µm)	Microstrain ( $\Delta d/d$ ) $ imes$ 10 <sup>6</sup>
C14 Hydride	a = 5.29824 c = 8.63854 Vol = 210.007 Å <sup>3</sup>	91	1.0	1000
NiZr	a = 3.31475 b = 9.96743 c = 4.13882 $Vol = 136.745 Å^{3}$	9	1.0	1000

#### Table 6

Lattice parameters, phase fraction, crystallite size, and isotropic microstrain of the phases obtained by Rietveld refinement for Zr33Cr22Mn15Fe25Ni5 alloy after hydrogenation at 296 K.

Phases	Lattice Parameters (Á)	Phase Fraction (wt.%)	Crystallite Size (µm)	Microstrain ( $\Delta d/d$ ) $ imes$ 10 <sup>6</sup>
C14 Hydride	a = 5.32227 c = 8.67505 Vol = 212.847 Å <sup>3</sup>	100	1.0	1000

state became even lower, which was undetectable to the X-ray diffraction.

Based on all the obtained results, the newly developed AB<sub>2</sub>-type High-Entropy Alloys (HEAs) demonstrated exceptional hydrogen storage capacity at room temperature, following a straightforward activation procedure. Both alloys exhibited rapid kinetics and almost complete reversibility at room temperature. It was observed that the hydrogen storage capacity is directly influenced by the extent of conversion from the C14 Laves phase to the C14 Laves hydride. In simpler terms, the quantity of NiZr present in the examined alloys could account for the variations in kinetic behavior and the maximum hydrogen capacity achieved. During the casting process, the intermetallic NiZr was found to be a competing phase with the available C14 phase. Consequently, a lower proportion of the intermetallic phase led to a higher availability of the C14 Laves phase, thereby enhancing the hydrogen storage properties of the material. It has been already shown [36,37] that the presence of secondary phases can reduce the hydrogen storage capacity in high entropy alloys. In a direct comparison with our previous investigation of the TiZrCrMnFeNi alloy [10], we could observe that the search for new alloys in the multi-element TiZrCrMnFeNi system by removing Ti and keeping the high proportion of Zr element can result in alloys with better H<sub>2</sub> storage properties. Despite the better H<sub>2</sub> storage performance at room temperature of the studied alloys in terms of reversible capacity, especially for Zr33Cr22Mn15Fe25Ni5 alloy, in comparison with the equiatomic TiZrCrMnFeNi (1.8 wt% and 1.22 H/M against to 1.7 wt% and 1.22 H/M) the new alloys can operate at very low pressures and the formation of hydride phase seems very stable at room temperature. This can be attested by looking at the plateau pressure in the PCT curves when it is typically lower than  $10^{-1}$  MPa [38–40]. Moreover, it is well known that some elements, such as Nb and Zr, exhibit negative mixing enthalpy, stabilizing the laves phases, which explains the good reversibility and good absorption at room temperature of the Zr-based alloys shown in this study [41].

#### 4. Conclusions

The novel AB<sub>2</sub> type HEAs - Zr<sub>33</sub>(CrMnFeNi)<sub>67</sub> and  $Zr_{33}Cr_{22}Mn_{15}Fe_{25}Ni_5$  - derived from the TiZrCrMnFeNi equiatomic alloy, reported in a previous study, were evaluated in the hydrogen storage properties by kinetics and PCT experiments. The alloys were selected with the aid of thermodynamic calculations employed by the CALPHAD method due to the high trend to be crystallized as a C14 Laves phase after removing the Ti and keeping the high proportion of Zr element in the compositions. The as-cast structure of both alloys could be well fitted by the crystal structures of hexagonal C14-type Laves and intermetallic NiZr phase. After full hydrogenation, it was observed the formation of C14 hydride stable at atmospheric pressure. At room temperature, the alloy Zr33(CrMnFeNi)67 absorbed 1.6 wt% and the Zr<sub>33</sub>Cr<sub>22</sub>Mn<sub>15</sub>Fe<sub>25</sub>Ni<sub>5</sub> absorbed 1.8 wt%. Either of them presented very fast kinetics and almost full reversibility without any complex activation process required. The superior performance of the Zr<sub>33</sub>Cr<sub>22</sub>Mn<sub>15</sub>Fe<sub>25</sub>Ni<sub>5</sub> could be explained by the higher amount of available C14 to be converted into hydride C14. Zr has claimed to have the ability to drop the equilibrium plateau pressure when present in higher concentration, due to the high hydrogen affinity.

#### Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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